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PATENT: 174PUS05579C

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF	:	E. MCINNIS, ET AL	
SERIAL NO.	:	09/213479	: GRP. ART UNIT:
FILED	:	17 December 1998	: EXAMINER:
FOR	:	HOT MELT ADHESIVES COMPRISING LOW FREE MONOMER, LOW OLIGOMER ISOCYANATE PREPOLYMERS	

WHICH IS A CONTINUATION OF:

IN RE APPLICATION OF	:	E. MCINNIS, ET AL	
SERIAL NO.	:	08/707,832	: GRP. ART UNIT: 1301
FILED	:	6 SEPTEMBER 1996	: EXAMINER: J. GALLAGHER
FOR	:	HOT MELT ADHESIVES COMPRISING LOW FREE MONOMER, LOW OLIGOMER ISOCYANATE PREPOLYMERS	

Assistant Commissioner for Patents
Washington, D.C. 20231

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Sir:

RULE 132 DECLARATION

I, Susan G. Musselman, residing at 1622 Chestertown Road, Allentown, PA hereby declare as follows:

1. I am employed by Air Products and Chemicals, Inc., the assignee of the invention described in the above-identified Application. I had been employed by Air Products and Chemicals, Inc. for 7 years in its Performance Chemicals Technology Group as an Applications Chemist actively working in the Polyurethane Specialty Products area. Presently I am in the Purchasing Department.

2. I have read and understand the Cody patent (US 5,075,407), which was relied upon by the Examiner in rejecting the claims pending in the above-identified Application.

3. In view of this reference the following experiments, which were performed under my direction while I was still in the Performance Chemicals Technology Group, are presented to compare the use of prepolymers made by reacting polyisocyanate with polyol in an NCO/OH equivalent ratio of about 2.1:1 as taught by Cody's Example 1 with prepolymers prepared at NCO/OH equivalent ratios of 6:1, 8:1 and 10:1. The "perfect" prepolymer and oligomer contents of the prepolymer reaction products were calculated Jeffrey Quay, a co-inventor of the above-identified application.

Example 1

80.3 g of 4,4'-diphenylmethane diisocyanate (MDI) were added to a 1 liter reactor and melted at 80°C. A polyol blend consisting of 288.6 g Dynacoll 7360 (OH# 30.5), 139.7 g Dynacoll 7230 (OH# 30.5) and 72.4 g Dynacoll 7110 (OH# 55) at 95°C was added to the reactor over 2 hours. The reaction temperature was held at 80°C overnight. As seen in the following Table the viscosity of the prepolymer reaction product was 48,000 cPs at 80°C. Reducing the residual isocyanate monomer content below 2% would only increase the viscosity.

Example 2

380.1 g of MDI were added to a 3 liter reactor and melted at 80°C. A polyol blend consisting of 288.0 g Dynacoll 7360 (OH# 30.5), 139.3 g Dynacoll 7230 (OH# 30.5) and 72.2 g Dynacoll 7110 (OH# 55) at 95°C was added to the reactor over 2 hours. The reaction temperature was held at 80°C overnight. Excess residual MDI was removed from the reaction product to a level of 0.4%.

Example 3

141.4 g of toluenediisocyanate (TDI) were added to a 3 liter reactor and heated to 50°C. A polyol blend consisting of 192.9 g Dynacoll 7360 (OH# 30.5), 93.3 g Dynacoll 7230 (OH# 30.5) and 48.4 g Dynacoll 7110 (OH# 55) at 95°C was added to the reactor over 2 hours. The reaction temperature was held at 50°C overnight. Excess residual TDI was removed from the reaction product to a level of <0.1%. Polyol blend OH# determined to be 38.0mg KOH/g.

Example 4

143.0 g of toluenediisocyanate (TDI) were added to a 3 liter reactor and heated to 50°C. A polyol blend consisting of 260.7 g Dynacoll 7360 (OH# 30.5), 126.0 g Dynacoll 7230 (OH# 30.5) and 65.3 g Dynacoll 7110 (OH# 55) at 95°C was added to the reactor over 2 hours. The reaction temperature was held at 50°C overnight. Excess residual TDI was removed from the reaction product to a level of <0.1%. Polyol blend OH# determined to be 38.0 mg KOH/g.

Example 5

136.8 g of 4,4'-diphenylmethane diisocyanate (MDI) were added to a 1 liter reactor and melted at 80°C. 900.0 g Ruco S105-30 hexanediol adipate (OH# 31.3) at 80°C was added to the reactor over 2 hours. The reaction temperature was held at 80°C overnight. As seen in the following Table the viscosity of the prepolymer reaction product was 42,250 cPs at 80°C. Reducing the residual isocyanate monomer content below 2% would only increase the viscosity.

Example 6

1234.3 g of MDI were added to a 3 liter reactor and melted at 80°C. 988.8 g Ruco S105-30 hexanediol adipate (OH# 31.3) at 80°C was added to the reactor over 2 hours. The reaction temperature was held at 80°C overnight. Excess residual MDI was removed from the reaction product to a level of <0.1%.

Example 7

354.2 g of toluenediisocyanate (TDI) were added to a 3 liter reactor and heated to 50°C. 912.5 g Ruco S105-30 hexanediol adipate (OH# 31.3) at 80°C was added to the reactor over 2 hours. The reaction temperature was held at 50°C overnight. Excess residual TDI was removed from the reaction product to a level of <0.1%.

Example 8

260.8 g of toluenediisocyanate (TDI) were added to a 3 liter reactor and heated to 50°C. 935.0 g Ruco S105-22 hexanediol adipate (OH# 22.4) at 80°C was added to the reactor over 2 hours. The reaction temperature was held at 50°C overnight. Excess residual TDI was removed from the reaction product to a level of <0.1%.

4. Evaluation of the prepolymers of Examples 1-8 are presented in the following Table:

Physical Property Determinations

Viscosity was measured using a Brookfield RV-DVIII viscometer with the Termosel attachment and a #21 spindle. Set to touch measured according to ASTM D1640 and Lap Shears were measured according to ASTM D1002. Melting and crystallization temperatures were determined using a TA MDSC 2929 from 0 to 150°C at 10°C/min. in heating mode and 150 to 0°C at 10°C/min. in cooling mode.

Oligomer and "Perfect" Prepolymer Content

The oligomer content was calculated using the following formula:

$$x = \frac{\%NCO/100 - \left(r * 42.02/E_I\right) - \left((1-r) * \left(\frac{42.02}{(2 * E_I) + (56100/OH\#)}\right)\right)}{\left(\frac{42.02}{(3 * E_I) + (2 * (56100/OH\#))}\right) - \frac{42.02}{(2 * E_I) + (56100/OH\#)}}$$

where:

x	oligomer weight fraction (x * 100% = oligomer wt. %)
%NCO	measured %NCO of prepolymer
r	residual isocyanate weight fraction
E_I	Diisocyanate equivalent weight (87.1 for TDI and 125 for MDI)
OH#	Measured OH# for polyol blend.

This formula makes the following assumptions:

1. All of the oligomer is 3:2 (3 isocyanate to 2 polyol molecules). This assumption will hold quite well when the overall level of oligomer is low (<20%) but as the oligomer level increases more higher oligomers (4:3, 5:4, etc.) are formed. The result is that the level of perfect prepolymer is underestimated and oligomer is overestimated. In the extreme as in Example 5 below the calculated oligomer level is greater than 100%.
2. No other side reactions are considered such as allophanate, isocyanurate, reaction with moisture to create urea, etc. The reaction conditions used in the examples are set to minimize the side reactions - low reaction temperature and protection against moisture contamination. However, TDI - polyester reactions are very susceptible to allophanate formation especially at the high NCO:OH ratios. Allophanate content was determined by NMR for Examples 3 and 4 to be on the order of 3-4 mole%, which would also explain the negative oligomer result for Example 3.
3. The reaction has gone to completion and there are no unreacted OH groups remaining.

The "perfect" prepolymer content was determined by subtracting the calculated oligomer content and the residue isocyanate monomer content from 100%.

Table

Example	1	2	3	4	5	6	7	8
Isocyanate	MDI	MDI	TDI	TDI	MDI	MDI	TDI	TDI
NCO/OH Ratio	2.1:1	10:1	8:1	6:1	2.15:1	10:1	8:1	8:1
Polyol OH# (mg KOH/g)	34.0	34.0	38.0	38.0	31.3	31.3	31.3	22.4
%NCO	2.17	2.27	2.57	2.52	2.03	1.99	2.19	1.56
Residual Isocyanate (wt%)	2.85	0.41	0.02	0.05	3.21	0.05	0.04	0.02
Calculated Oligomer (wt%)	88	7	-1	4	104	8	-3	2
"Perfect" Prepolymer (wt%)	9	93	100	96	0	92	100	98
Viscosity(cPs)								
@ 80°C	48000	12600	5524		42250	6350	4571	10828
@ 90°C	27875	8125	3484		28500	--	3161	7435
@ 110°C	11800	3450	1579		14188	2142	1681	3960
@ 120°C	8000	2600	1164		10500	1613	--	3236
Thermal Properties DSC								
Melt (°C)	49.8	51.0	43.3	52.3	55.5	56.5	56.7	58.9
Crystallization (°C)	15.7	23.0	23.4	23.4	21.7	30.6	28.0	26.5
Adhesive Properties								
Tack Free (minutes)	3.5	1.5	2.5	ND	3.0	0.5	1.0	1.0
Lap Shear (psi)								
Metal								
2 hrs	244	232	232	288	436	332	361	503
1 day	371	304	277	383	566	442	440	654
2 day	388	316	296	408	667	528	413	636
5 day	466	378	319	421	1069	1069	495	937
7 day	528	409	330	454	1094	1061	540	1113
Wood								
2 hrs	318	318	201	248	606	454	214	375
1 day	919	753	259	281	1168	881	374	600
2 day	1106	1120*	322	587	1442	1592*	449	831
5 day	959	1253*	535	966	1623*	Substrate Failure	906	1331*
7 day	1025	1118*	1028	ND	1619*	Substrate Failure	1400*	1492*

* Some Substrate Failure- 1-2 Samples out of 5
ND = No data

4. Example 1 is essentially Cody's Example 1 and Example 5 is essentially a standard reactive hot melt without any additives. The prepolymer reaction products of Examples 1 and 5 contained residual isocyanate monomer at >2.5 wt% and had viscosities >40,000 cPs at 80°C. If the residual isocyanate monomer were removed by distillation to <2 wt%, the viscosities would be even higher, the excess isocyanate monomer having a

diluent effect. Example 2 material having a viscosity of 8125 cPs at 90°C could be processed at that temperature whereas to use the Example 1 material would require a process temperature of 120°C.

I hereby declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that the statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Susan G. Musselman

Susan G. Musselman

1/20/99

Date